ISSN 2250-3153

OPTICAL BAND GAP STUDIES OF POLYPYRROLE DOPED WITH CUZnFe2O4 NANO PARTICLES

***V.S. Shanthala [1], S.N. Shobha Devi [2], M. V. Murugendrappa [3]**

[1]The Oxford College of Science,Department of Physics, Bangalore, India
[1]Department of Research and studies in Physics, Tumkur University, Tumkur, India
shanthalasastry@gmail.com cell-9880820145
[2]Department of Physics, BMS College for Women, Bangalore, India
drshobhasn@gmail.com cell-9845914272
[3]Department of Physics, BMS College of Engineering, Bangalore, India
murugeshbms@gmail.com cell-9972727000
*corresponding Author : shanthalasastry@gmail.com

Abstract- *Polypyrrole/$CuZnFe_2O_4$ nanocomposites were synthesized by in-situ polymerization with Ammonium persulphate as an oxidising agent. Optical band gap of chemically synthesized polypyrrole and Polypyrrole-$CuZnFe_2O_4$ (10% - 50%) nanocomposites have been studied at room temperature and normal pressure. Energy band gap of these materials are determined by UV-VIS absorption spectra in the wavelength range 264nm–1936nm by spectrophotometer. In this work the experimental results obtained from the UV-VIS spectra are reported for nanocomposites of different wt percentages (10% -50%.). Characteristic peak around 800 nm was observed in all the nanocomposites confirming the formation of polypyrrole. The work highlights the optical properties of these polymer nanocomposites for making them a suitable candidate for optoelectronic devices*

Keywords: Polypyrrole, band gap, absorption spectra, nanocomposite, wavelength.

I. Introduction

In recent years Polymer nanocomposites have become one of the most extensively studied materials all over the world due to their unusual properties. Owing to their unusual combination of properties they have wide range of applications in various fields such as sensors, electronic devices, memory devices, lithium batteries, energy storage, microwave absorbers, electromagnetic shielding, optoelectronic devices etc.; [1-2]. In a number of applications the control of band gap is essential, be it for light emitting diodes (LED) transparency in the visible region combined with high electrical conductivity etc.[3]. The optical band gap is the characteristic of the materials and it depends on the crystallinity and stoichiometry of the material. UV–VIS diffuse reflectance spectroscopy is one of the most employed characterization technique that describes the electronic behavior present in the structure of the solid. Through the absorption spectra, UV–VIS spectroscopy gives information about the electronic transitions of the different orbitals of a solid. The optical excitation of the electrons from the valence band to the conduction band is evidenced by an increase in the absorbance at a given wavelength, which corresponds to the band gap energy.

Polypyrrole (PPy) is one of the most attractive conducting polymers due to its special transport properties, facile synthesis, tunable conductivity and good environmental stability [4]. Nano crystalline ferrites are materials of considerable interest due to their unique dielectric, magnetic and optical properties. Nanocrystalline Spinel copper zinc ferrites ($CuZnFe_2O_4$) have been extensively investigated due to their potential applications in non-resonant device, radio frequency circuits, rod antennas, high quality filters and transformer core [5]. In this work we report optical band gap of pure Polypyrrole and polypyrrole doped with copper zinc iron oxide ($CuZnFe_2O_4$) nanoparticles

2. Materials and Methods.

Chemicals – The monomer Pyrrole, oxidising agent Ammonium per sulphate, acetone and nanoparticle Copper zinc iron oxide ($CuZnFe_2O_4$) were purchased from Sigma Aldrich. The particle size of $CuZnFe_2O_4$ is < 100nm. All the chemicals were of analytical grade and used as received without any further treatment.

2.1. Synthesis of Polypyrrole

PPy was synthesized by in-situ polymerization of monomer Pyrrole in the presence of oxidising agent ammonium persulphate. 0.3M pyrrole taken in a round bottomed glass flask was placed in an ice tray mounted on a magnetic stirrer. 0.6M Ammonium persulphate was added drop wise using a burette to the above 0.3M Pyrrole. The reaction was carried out for 5 hours under continuous stirring maintaining temperature of 0 to 5 degree Celsius. The resulting precipitate was removed by filtration by suction. The Polypyrrole powder thus obtained was then dried in a hot air oven and subsequently in a muffle furnace at a temperature of 100 degree Celsius. The yield was 2.15 g, taken as 100wt. %

2.2. Synthesis of Ppy/ $CUZnFe_2O_4$ Nanocomposites.

PPy/$CuZnFe_2O_4$ nanocomposites were synthesized by the same method. For 0.3M Pyrrole solution, 0.215 g (10wt.%) of $CuZnFe_2O_4$ was added and mixed thoroughly in a round bottomed flask. O.6M ammonium persulphate was added drop-wise with the help of burette to the above solution and the entire procedure is repeated to get 10wt.% composite. Similarly 0.43g, 0.60g, 0.86g, 1.07g of nanoparticles are taken and the entire procedure is repeated to get 20, 30, 40 and 50wt.% PPy/ $CuZnFe_2O_4$ nanocomposites.. The immiscibility of heterophases of the polymer and $CuZnFe_2O_4$ constituents has been resolved by ultrasonicating the mixture, which has ensured the homogeneous dispersion of nanoparticles in the polymer matrix[6].

2.3 UV-VIS Spectroscopy Measurements.

The optical properties of the nanocomposites were studied using UV-Vis spectrometry. The optical absorption data of the polymer samples were recorded in the range of 264 nm to 1936 nm by using *Cary 300* spectrophotometer.

ISSN 2250-3153

3. Results and Discussions

UV-VIS spectra of PPy and PPy-$CuZnFe_2O_4$ nanocomposites are shown in Fig.1. A major peak at 800 nm was observed for pure (undoped) Polypyrrole which is attributed to ∏-∏* inter band transitions and is characteristic peak of conducting polypyrrole. Small humps in the spectrum indicates polaron bipolaron transitions for all the samples. A shift in characteristic wavelength is observed after doping. The shift is very small for all nanocomposites except for nanocomposites of 30% which has shifted from 804nm to 765nm. These observed shifts are due to dopant-polymer interaction[7,11].

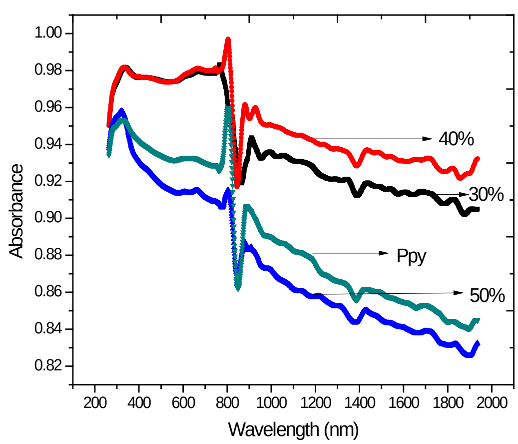


Fig.1 UV-VIS spectra

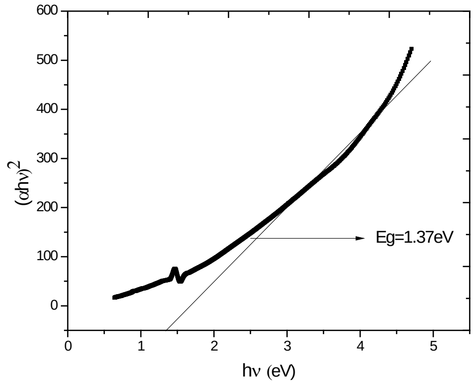


Fig.2a. Tauc's Plot.of Ppy

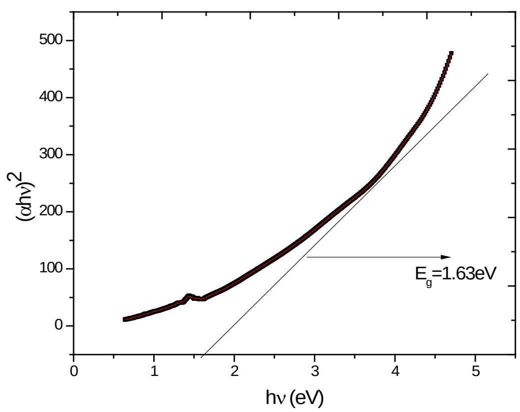


Fig.2b. Tauc's Plot of PPy / 30%

The energy gap Eg can be determined by applying the Kubelka–Munk (K–M) method. The K–M method is based on the following equation

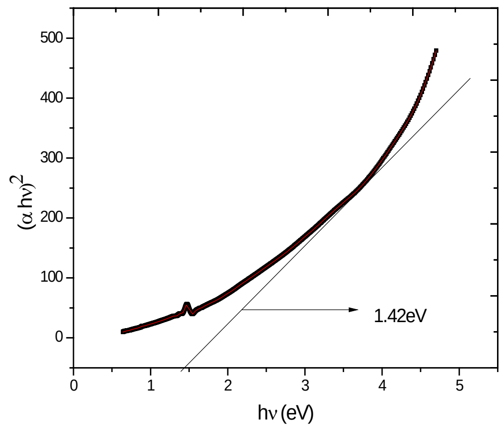


Fig.2c. Tauc's Plot of PPy / 40%

$\alpha = \frac{(1-R)^2}{2R}$, where 'R, is the reflectance; It can be seen from the graph that the absorbance changes with the addition of nanoparticles for nanocomposites of 30% and 40%, there is an increase in the absorbance but decrease in the absorbance is observed for nanocomposites of 50%, which results in variation in the energy gap. The energy band gap of these materials has been calculated with the help of Tauc plots shown in Fig.2. The energy gap is calculated by relation,

$\alpha h\nu = A [h\nu - Eg]^n$ where n= ½ or 2 .For direct band gap materials it is 1/2 and for indirect gap materials it is 2 Here it is taken as 2.

Fig.2a,2b,2c,2d and 2e shows the plots of $(\alpha h\nu)^2$ v/s hν.(Tauc plots) for PPy, PPy/30%, PPy/40% and PPy/50%. The band gaps of PPy and PPy-nanocomposites were determined by extrapolation of the plot of $(\alpha h\nu)^2$ v/s hν, Extrapolation of the line to the x-axis where the value of $(\alpha h\nu)^2$ is zero, Considering indirect transitions, the values obtained for E_g were 1.37 eV for PPy, which was in good agreement with the results obtained. 1.32ev for nanocomposites of 10% , 1.55eV for 20%, 1.63eV for 30%, 1.42eV for 40% and 1.40eV for 50% [8-10]

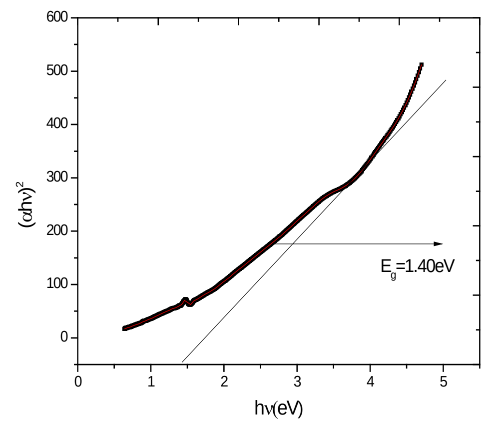


Fig.2d Tauc's Plot for (50%

The refractive index ,n, can be calculated using the relation $n = 3.3668 (Eg)^{-0.32234}$ [11]. The calculated values of energy gap and Refractive index are given in Table 1.

Table1. Energy gap (Eg) and Refractive index (n)

SL.No	Nanocomposites	Eg (eV)	Refractive Index (n)
1	0% (pure Ppy)	1.37	3.0419
2	10%	1.32	3.0785
3	20%	1.55	2.9231
4	30%	1.63	2.8762
5	40%	1.42	3.0069
6	50%	1.40	3.0207

4 Conclusions:

The work highlights the determination of optical properties - band gap and Refractive index of nanocomposites using UV-VIS spectra. Characteristic peak around 800 nm was observed in all the nanocomposites confirming the formation of polypyrrole. The energy gap was determined using Tauc's plots. The results revealed that the band gap of the polypyrrole changes on doping with nanoparticles, The band gap of pure PPy was found to be 1.37eV. The nanocomposites of 30wt.% have highest band gap (1.63eV) and low refractive index (2.8762) among all nanocomposites. The nanocomposites of 20wt.% have lowest band gap (1.32eV) and highest refractive index (3.0785) among all nanocomposites. The optical properties of this polymer nanocomposites make them a suitable candidate for optoelectronic devices .

Acknowledgements

The authors would like to acknowledge Dr. Mallikarjuna Babu, Principal, B.M.S. College of Engineering Bangalore and Dr. Pranesha T.S., HOD, Dept. of Physics, B.M.S.C.E., Bangalore for their support in carrying out this work.

References:

1. DR Paul, LM Robeson *Polymer(2008),* Vol. 49 : 3187-3204

2. H Arami, M Mazloumi, R Khalifehzadeh, S Hojjati Emami, SK Sadrnezhaad *Materials Letters*. (2007) Vol. 61: 4412- 4415

3 V.Shaktawat, N. Jain, R. Saxena, N. S. Saxena, T. P. Sharma, Electrical conductivity and optical band gap studies of polypyrrole doped with different acids, *Journal of optoelectronics and advanced materials* (2007)Vol. 9, No. 7: 2130 – 2132

4. Ritu P. Mahare, Devendra K. Burghate, Subhash B. Kondawar, (2014) Development of nanocomposites based on polypyrrole and carbon nanoyubes for supercapacitors, *Adv.Mat.Lett.*,Vol..5(7) 400-405.

5. Anjaneyalu, P.Narayana Murthy, Sk.Md.Rafi, Sk.Bademiya, G. Samuel John, Effect on magnetic properties of zinc doped nano ferrites synthesized by precursor or method, *International letters of Chemistry, Physics and Astronomy* , ISNN:2299-3843, Vol.19:37-43

6. V.S. Shanthala, S.N. Shobha Devi, M. V. Murugendrappa, Thermal Studies of Polypyrrole - $NiZnFe_2O_4$ Nanocomposites , *International journal of InnovativeResearch in Technology,* (2016) Vol. 3 Issue 1, 198-203

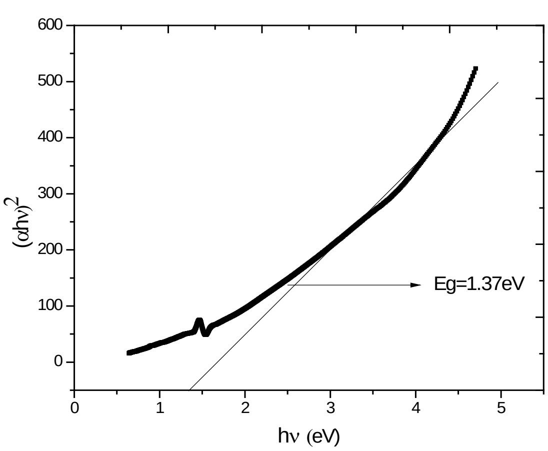
7 Mahnaz M. Abdi, H.N.M. Ekramul Mahmud, Luqman Chuah Abdullah, Anuar Kassimc, Mohamad Zaki Ab. Rahman and Josephine Liew Ying Chyi, Optical band gap and Conductivity measurements of Polypyrrole-Chitosan composite thin films. *Chinese Journal of Polymer Science* (2012)Vol. 30, No. 1, 93-100.

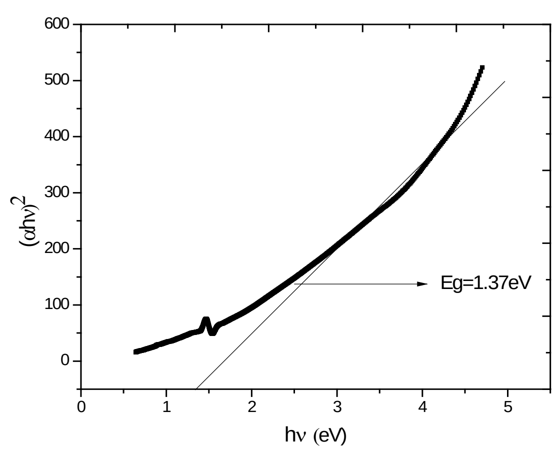
8 Rosendo Lo´pez Ricardo Go´mez, Band-gap energy estimation from diffuse reflectance measurements on sol–gel and commercial TiO2: a comparative study, *J Sol-Gel Sci. Technol* (2012) Vol.61:1–7

9. Nader Ghobadi, Band gap determination using absorption spectrum fitting procedure, *Ghobadi International Nano Letters* (2013) Vol.3:1-4

10. Eunah KIM, Zhong-Tao, JIANG and Kwangsoo NO, Measuremnt and calculation of optical band gap of Chromium Aluminium Oxide films *Jpn. J.of Applied Physics* (2000) Vol.39:4820-4825.

11. B S. Chakrabarty *Int. Journal of Engineering Research and Applications* ISSN : 2248-9622(2013) Vol.3 Issue 6: 888-890





www.ijsrp.org